

ELECTROFORMATION AND GROWTH OF SALT FILMS ON LEAD

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Salt film formation during the anodic polarization of active metals is a relevant phenomenon in many electrochemical processes such as electrochemical machining, electrolytic polishing and corrosion. Much work has been done in the past on the composition and electrochemical behaviour of the anodic films formed on lead electrodes in sulphuric and other acidic electrolytes. However, the kinetics and mechanism leading to the formation of the passive layers as well as the electroreduction process are still open to discussion [1-3]. Previous studies on the electrochemical properties of lead electrodes in aqueous HCl solutions indicate that the overall reaction leading to passivation is the formation of a layer of PbCl_2 being the diffusion of chloride ions to the electrode surface the limiting factor in the formation of the passive layer [4].

In this work the active to passive transition of lead electrodes in solutions containing chloride is described and it will be shown that a poorly conducting salt film is formed involving different overpotential contributions with a predominant ohmic resistance control at high surface coverages. The working electrode consisted of a polycrystalline lead rod (99.9999% purity) polished mechanically with emery paper.

The j/E potentiodynamic profiles show during the positive potential scan an anodic current peak in the -0.5 to -0.3 V potential range which is attributed to the formation of the PbCl_2 layer followed by a more or less sharp decrease in current due to the fact that the salt layer is insulating or poorly conducting and produces electrode passivation. The current density remains low until *ca.* 2.2V where breakdown of the anodic film with simultaneous oxygen evolution takes place. In the negative scan the current density is very low in a wide potential range and at -0.6 V, the electroreduction of the anodic film occurs.

Potentiodynamic curves taken at different sweep rates show that the j/E response has the same general shape and that there is a potential range where a linear j/E behaviour for the anodic as well as for the cathodic processes is obtained. Also, peak current density and peak potential for both the anodic and the cathodic current peaks were found to vary linearly with the square root of sweep rate, being a clear indication that the rate of the overall processes is controlled by a resistive process [5-8]. The early stages of electroformation of the salt layer also involve soluble species formation and a nucleation step.

The potentiodynamic results were explained through the layer-pore resistance model [5-8]. According to this model, the passivating layer grows and spreads across the surface until only small pores in the layer remain and the rate of the current flow is controlled by the resistance of the electrolyte in the pores. The potentiodynamic j/E profiles for a film growing under

resistance control should exhibit a maximum current and the curves obtained at different sweep rates should have the same shape, characterized by a linear portion in the rising part of the current peak. After the maximum, the current should show a sharp decrease and the final value is dependent on film conductivity and surface coverage. Experimental potentiodynamic profiles obtained under different experimental conditions were compared with theoretical curves calculated using the model and the characteristic parameters of the porous layer were obtained. The excellent agreement of the experimental data with the model gives an additional evidence that growth of the salt film is mainly controlled by the resistance of the pore-layer system.

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